

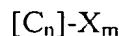
## CLAIMS

5 1. A functionalized carbon nanotube, the surface of which carries covalently bound reactive and/or activable functional groups which are homogeneously distributed on said surface, said functionalized carbon nanotube being substantially intact and soluble in organic and/or aqueous solvents.

10 2. A functionalized carbon nanotube according to claim 1, wherein said carbon nanotube is a single-walled (SWNT) or a multi-walled carbon nanotube (MWNT).

15 3. A functionalized carbon nanotube according to claim 2, wherein the organic solvents are selected from a group comprising dimethylformamide, dichloromethane, chloroform, acetonitrile, dimethylsulfoxide, methanol, ethanol, toluene, isopropanol, 1,2-dichloroethane, N-methylpyrrolidone, tetrahydrofuran.

15 4. A functionalized carbon nanotube according to claim 3, of following general formula:



wherein:

20  $C_n$  are surface carbons of a substantially cylindrical carbon nanotube of substantially constant diameter, said diameter being from about 0.5 to about 50 nm, in particular from about 0.5 to 5 nm for SWNTs and from about 20 to about 50 nm for MWNTs,

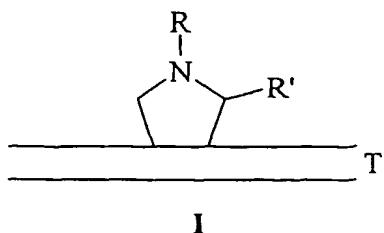
X is a functional group,

n is an integer from about  $3 \cdot 10^3$  to about  $3 \cdot 10^6$ ,

25 m is an integer from about  $0.001n$  to about  $0.1n$ ,

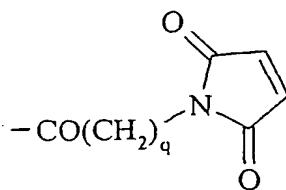
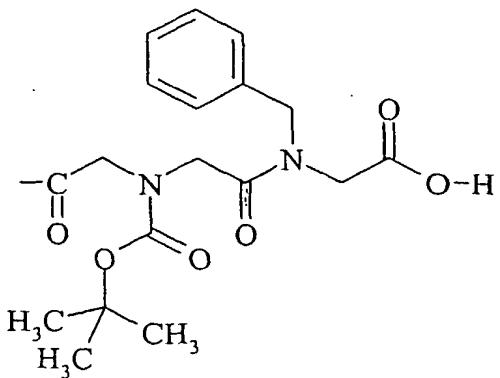
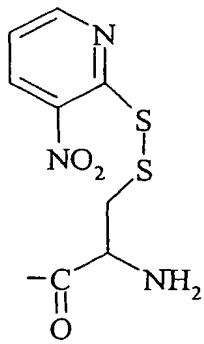
there are from about  $2 \cdot 10^{-11}$  moles to about  $2 \cdot 10^{-9}$  moles of X functional groups per  $cm^2$  of carbon nanotube surface.

30 5. A functionalized carbon nanotube according to claim 4, wherein X is a pyrrolidine ring, of the following general formula (I):



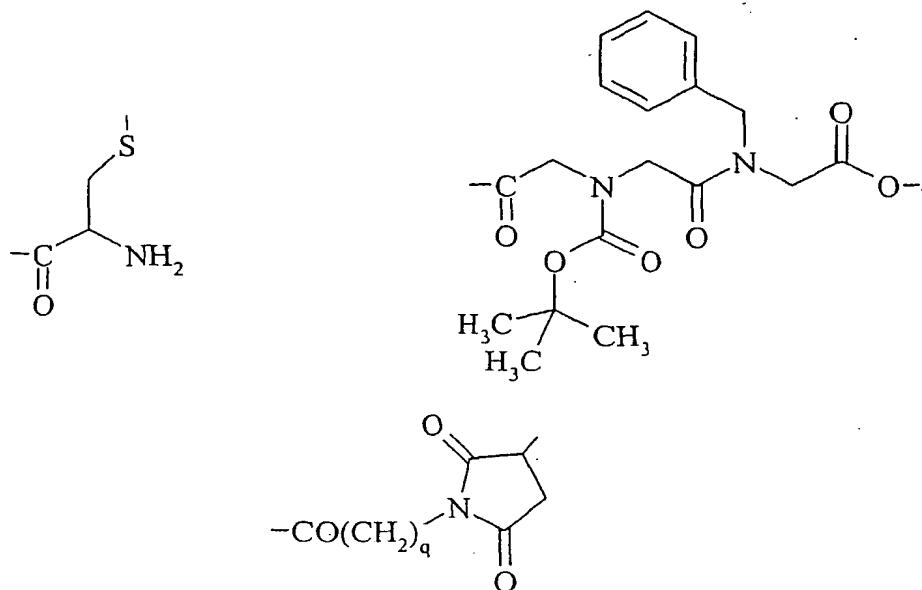
wherein T represents a carbon nanotube, and independently from each other R and R' represent -H or a group of formula -M-Y-(Z)<sub>a</sub>-(P)<sub>b</sub>, wherein independently from each other a and b represent 0 or 1, provided R and R' cannot simultaneously represent H, and:

- M is a spacer group from about 1 to about 100 atoms, such as a group selected from the list comprising  $-(CH_2)_r-$  or  $-(CH_2-CH_2-O)_r-CH_2-CH_2-$ , wherein r is an integer from 1 to 20;
- Y is a reactive group when a=b=0, such as a group selected from the list comprising  $-OH$ ,  $-NH_2$ ,  $-COOH$ ,  $-SH$ ,  $-CHO$ , a ketone such as  $-COCH_3$ , an azide or a halide; or derived from a reactive group, when a or b is different from 0, such as a group selected from the list comprising  $-O-$ ,  $-NH-$ ,  $-COO-$ ,  $-S-$ ,  $-CH=$ ,  $-CH_2-$ ,  $-CC_kH_{2k+1}=$ , wherein k is an integer from 1 to 10, in particular  $-CCH_3=$ , or  $-CHC_kH_{2k+1}-$ , wherein k is an integer from 1 to 10, in particular  $-CHCH_3-$ ;
- Z is a linker group, liable to be linked to a P group, and if need be to release said P group, such as a group of one of the following formulae when a=1 and b=0:



wherein  $q$  is an integer from 1 to 10;

or of one of the corresponding following formulae when  $a=1$  and  $b=1$ :

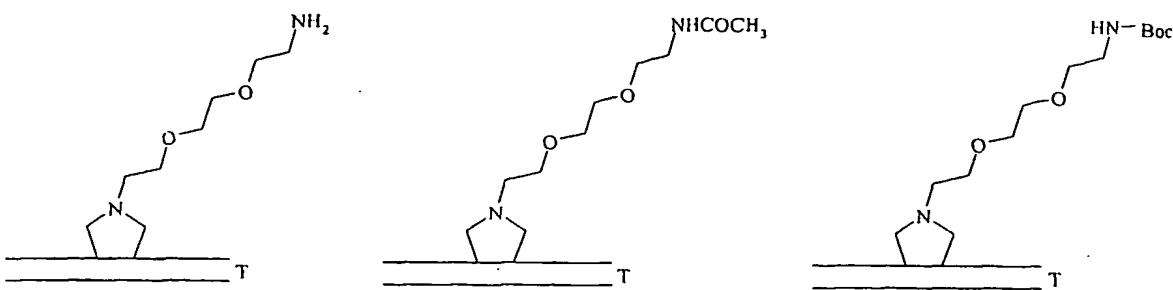


wherein  $q$  is an integer from 1 to 10;

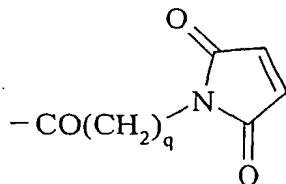
- P is an effective group allowing spectroscopic detection of said functionalized carbon nanotube, such as a fluorophore, such as FITC, or an active molecule, liable to induce a biological effect, such as an amino acid, a peptide, a pseudopeptide, a protein, such as an enzyme or an antibody, a nucleic acid, a carbohydrate, or a drug.

if appropriate at least one of Y, Z, or P groups, can be substituted by a capping group, such as  $\text{CH}_3\text{CO}-$  (acetyl), methyl, or ethyl, or a protecting group such as methyl, ethyl, benzyl, *tert*-butyl, trityl, 3-nitro-2-pyridylsulfenyl, *tert*-butyloxycarbonyl (Boc), fluorenylmethyloxycarbonyl (Fmoc), benzylcarbonyl, trimethylsilylethyoxy carbonyl, phtalimide, dimethylacetal, diethylacetal or, 1,3-dioxolane.

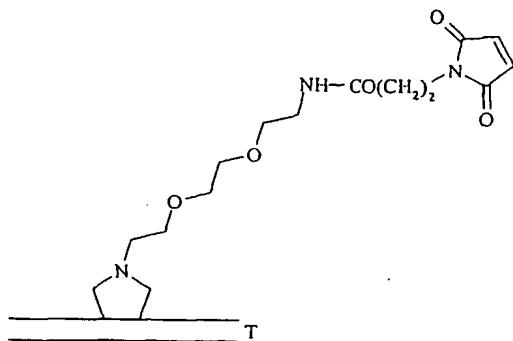
6. A functionalized carbon nanotube according to claim 5, wherein  $a=b=0$  and Y is a reactive group selected from the list comprising -OH, -NH<sub>2</sub>, -COOH, -SH, -CHO, a ketone, such as -COCH<sub>3</sub>, an azide, or a halide, in particular -NH<sub>2</sub>, said functionalized carbon nanotube being, if appropriate, substituted by a capping or a protecting group, such as defined in claim 5, in particular a Boc or acetyl group, and being for instance a functionalized carbon nanotube of one of the following formulae:



7. A functionalized carbon nanotube according to claim 5, wherein  $a=1$  and  $b=0$ ,  $Y$  is derived from a reactive group and selected from the list comprising  $-O-$ ,  $-NH-$ ,  $-COO-$ ,  $-S-$ ,  $-CH=$ ,  $-CH_2-$ ,  $-CC_kH_{2k+1}-$ , wherein  $k$  is an integer from 1 to 10, in particular  $-CCH_3=$ , or  $-CHC_kH_{2k+1}-$ , wherein  $k$  is an integer from 1 to 10, in particular  $-CHCH_3-$ , and  $Z$  is as defined in claim 5 and represents in particular the group of the following formula:

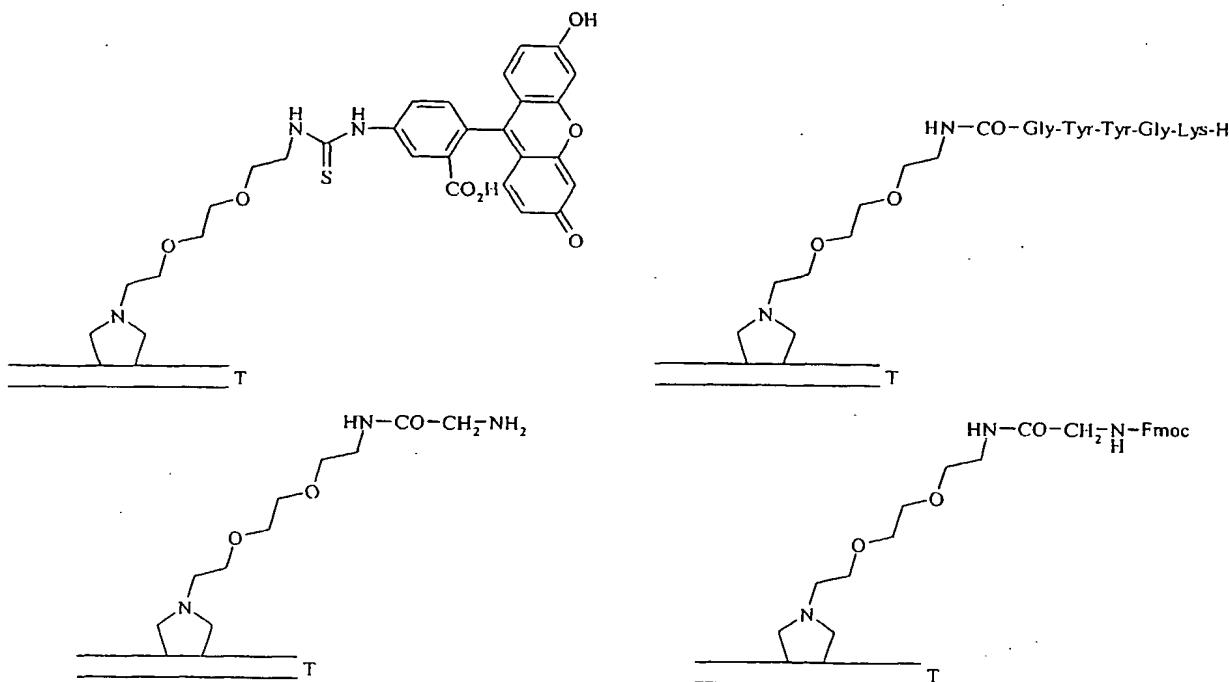


5  
10  
15  
wherein  $q$  is an integer from 1 to 10, said functionalized carbon nanotube being if appropriate substituted by a protecting group, such as defined in claim 5, and being for instance the functionalized carbon nanotube of the following formula:



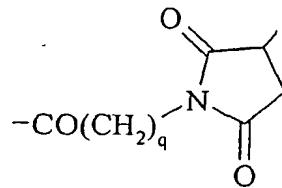
8. A functionalized carbon nanotube according to claim 5, wherein  $a=0$  and  $b=1$ ,  $Y$  is derived from a reactive group and selected from the list comprising  $-O-$ ,  $-NH-$ ,  $-COO-$ ,  $-S-$ ,  $-CH=$ ,  $-CH_2-$ ,  $-CC_kH_{2k+1}-$ , wherein  $k$  is an integer from 1 to 10, in particular  $-CCH_3=$ , or  $-CHC_kH_{2k+1}-$ , wherein  $k$  is an integer from 1 to 10, in particular  $-CHCH_3-$ , and  $P$  is an effective group or an active molecule, such as defined in claim 5, in particular FITC, an amino acid, such as glycine, or a peptide,

such as the peptide H-Lys-Gly-Tyr-Tyr-Gly-OH, said functionalized carbon nanotube being if appropriate substituted by a protecting group as defined in claim 5, such as Fmoc, and being for instance a functionalized carbon nanotube of one of the following formulae:



5

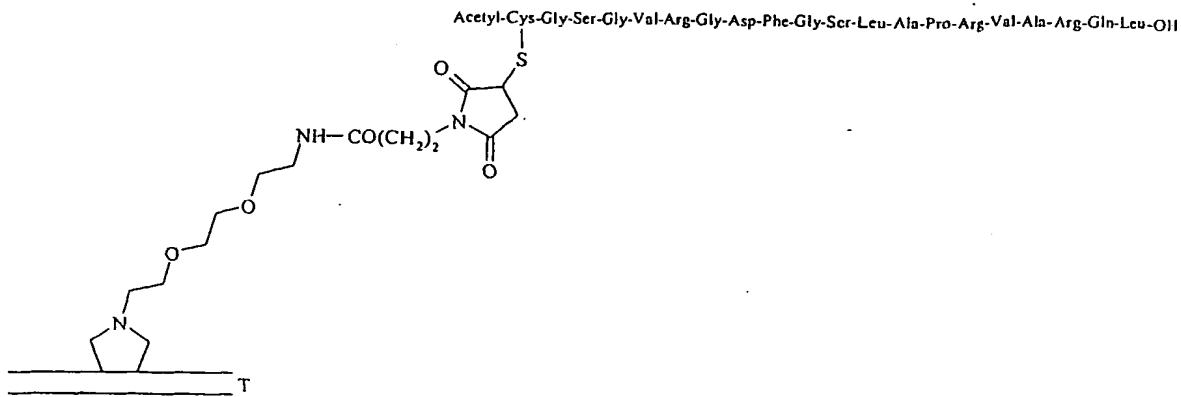
9. A functionalized carbon nanotube according to claim 5, wherein  $a=1$  and  $b=1$ ,  $Y$  is derived from a reactive group and selected from the list comprising  $-O-$ ,  $-NH-$ ,  $-COO-$ ,  $-S-$ ,  $-CH=$ ,  $-CH_2-$ ,  $-CC_kH_{2k+1}-$ , wherein  $k$  is an integer from 1 to 10, in particular  $-CCH_3-$ , or  $-CHC_kH_{2k+1}-$ , wherein  $k$  is an integer from 1 to 10, in particular  $-CHCH_3-$ ,  $Z$  is as defined in claim 5 and represents in particular the group of the following formula:



10

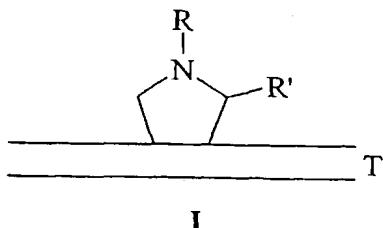
wherein  $q$  is an integer from 1 to 10, and  $P$  is as defined in claim 5, in particular a peptide, such as the peptide Acetyl-Cys-Gly-Ser-Gly-Val-Arg-Gly-Asp-Phe-Gly-Ser-Leu-Ala-Pro-Arg-Val-Ala-Arg-Gln-Leu-OH, said functionalized carbon nanotube being if appropriate substituted by a protecting group, such as defined in claim 5, and being for instance the functionalized carbon nanotube of the following formula:

15



10. A functionalized carbon nanotube according to claim 8 or 9, wherein P is a peptide or  
 5 a protein, said peptide or protein comprising in particular a B cell epitope or a T cell epitope, such as a T helper epitope or a T cytotoxic epitope, or a mixture thereof.

11. A process for preparing a functionalized carbon nanotube of the following formula I:



I

wherein T represents a carbon nanotube and independently from each other R and R' represent -H or a group of formula -M-Y, provided R and R' cannot simultaneously represent H, wherein:

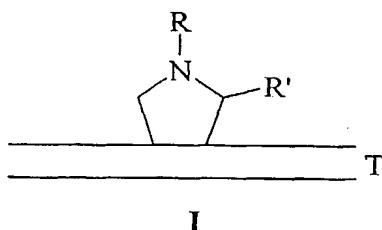
- -M- is a spacer group from about 1 to about 100 atoms, such as a group selected from the list comprising  $-(CH_2)_r-$  or  $-(CH_2-CH_2-O)_r-CH_2-CH_2-$ , wherein r is an integer from 1 to 20;
- -Y is a reactive group, such as a group selected from the list comprising, -OH, -NH<sub>2</sub>, -COOH, -SH, -CHO, a ketone such as -COCH<sub>3</sub>, an azide, a halide, if appropriate protected, such as -O-Q, -NH-Q, -COO-Q, -S-Q, -CH(OQ)<sub>2</sub>,  

$$\begin{array}{c} \text{---C---} \\ \text{O---Q} \end{array} \quad \text{wherein } k \text{ is an integer from 1 to 10, in particular } \begin{array}{c} \text{---C---} \\ \text{---CH}_3 \\ \text{O---Q} \end{array}$$
,  
 20 wherein Q is a protecting group or forms a protecting group with the adjacent atoms to which it is linked;

said process comprising the following step:

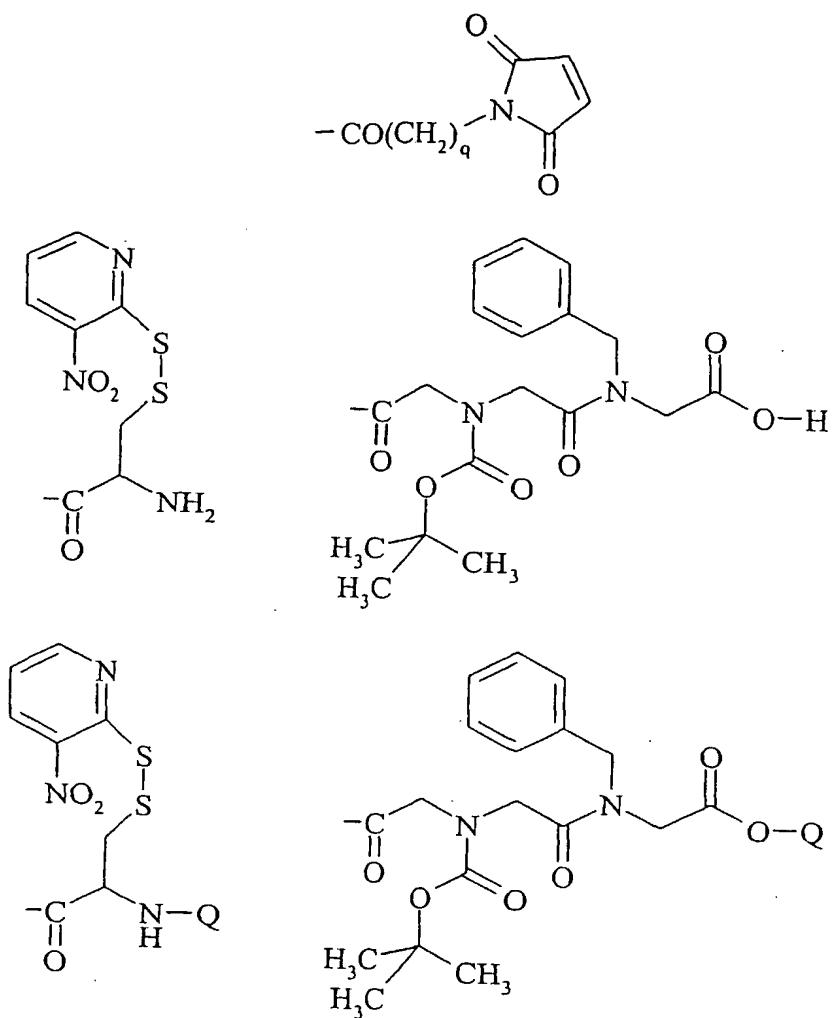
- adding, to a carbon nanotube, the compounds  $R'-CHO$  and  $R-NH-CHR''-COOR'''$  by a 1,3-dipolar cycloaddition, wherein:
  - $R$  and  $R'$  are as defined above;
  - $R''$  is  $-H$  or an amino acid side-chain;
  - $R'''$  is  $-H$ , an alkyl group of 1 to 5 carbon atoms, a  $(CH_2CH_2O)_t-CH_3$  group, wherein  $t$  is an integer from 1 to 20; or an aromatic group;
- to obtain a functionnalized carbon nanotube of formula I, if appropriate protected;
- if necessary, deprotecting the functionalized carbon nanotube of formula I, to obtain an unprotected functionalized carbon nanotube of formula I.

10 12. A process for preparing a functionalized carbon nanotube of the following formula I:



15 wherein  $T$  represents a carbon nanotube and independently from each other  $R$  and  $R'$  represent  $-H$  or a group of formula  $-M-Y-Z$ , provided  $R$  and  $R'$  cannot simultaneously represent  $-H$ , wherein:

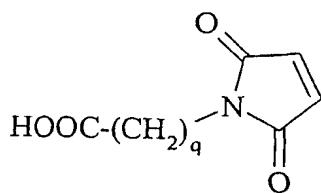
- $-M-$  is a spacer group from about 1 to about 100 atoms, such as a group selected from the list comprising  $-(CH_2)_r-$  or  $-(CH_2-CH_2-O)_r-CH_2-CH_2-$ , wherein  $r$  is an integer from 1 to 20;
- $-Y-$  is a group derived from a reactive group, such as a group selected from the list comprising,  $-O-$ ,  $-NH-$ ,  $-COO-$ ,  $-S-$ ,  $-CH=$ ,  $-CH_2-$ ,  $-CC_kH_{2k+1}=$ , wherein  $k$  is an integer from 1 to 10, in particular  $-CCH_3=$ , or  $-CHC_kH_{2k+1}-$ , wherein  $k$  is an integer from 1 to 10, in particular  $-CHCH_3-$ ;
- $-Z$  is a linker group, liable to be linked to a  $P$  group, and if need be to release said  $P$  group, if appropriate protected by a capping or a protecting group  $-Q$ , such as a group of one of the following formulae:

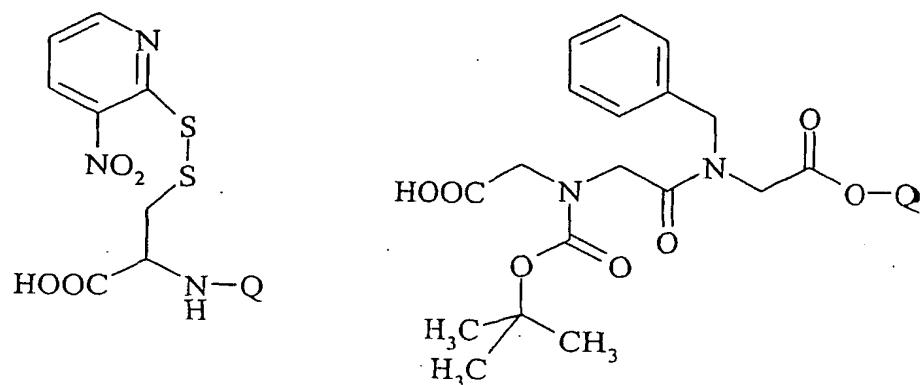


wherein q is an integer from 1 to 10;

said process comprising the following steps:

- adding to a unprotected functionalized carbon nanotube of formula I according to claim 11 a linker group of formula Z, if appropriate protected by a capping or a protecting group -Q, such as a group of one of the following formulae:





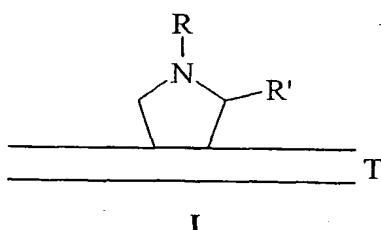
wherein  $q$  is an integer from 1 to 10;

to obtain a functionalized carbon nanotube of formula I, if appropriate protected;

- if necessary, deprotecting the functionalized carbon nanotube of formula I, to obtain an unprotected functionalized carbon nanotube of formula I

5

13. A process for preparing a functionalized nanotube of the following formula I:



wherein T represents a carbon nanotube and independently from each other R and R' represent -H or a group of formula -M-Y-Z-P or of formula -M-Y-P, provided R and R' cannot simultaneously represent -H, wherein:

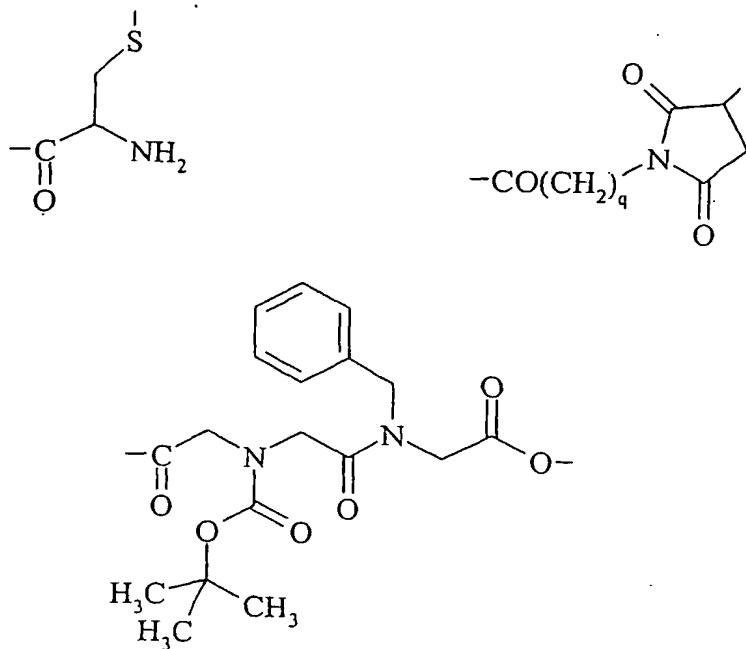
10 wherein T represents a carbon nanotube and independently from each other R and R' represent -H or a group of formula -M-Y-Z-P or of formula -M-Y-P, provided R and R' cannot simultaneously represent -H, wherein:

15

- -M- is a spacer group from about 1 to about 100 atoms, such as a group selected from the list comprising  $-(CH_2)_r-$  or  $-(CH_2-CH_2-O)_r-CH_2-CH_2-$ , wherein r is an integer from 1 to 20;
- -Y- is a group derived from a reactive group, such as a group selected from the list comprising, -O-, -NH-, -COO-, -S-, -CH=,  $-CH_2-$ ,  $-CC_kH_{2k+1}=$ , wherein k is an integer from 1 to 10, in particular  $-CCH_3=$ , or  $-CHC_kH_{2k+1}-$ , wherein k is an integer from 1 to 10, in particular  $-CHCH_3-$ ;
- -Z- is a linker group, liable to be linked to a P group, and if need be to release said P group, such as a group of one of the following formulae:

15

20



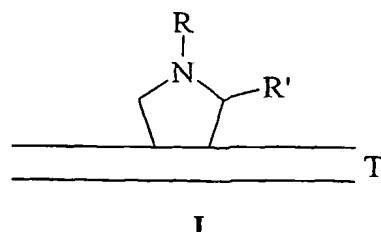
wherein q is an integer from 1 to 10;

- -P is an effective group allowing spectroscopic detection of said functionalized carbon nanotube, such as a fluorophore, such as FITC, or an active molecule, liable to induce a biological effect, if appropriate protected, such as an amino acid, a peptide, a pseudopeptide, a protein, such as an enzyme or an antibody, a nucleic acid, a carbohydrate, or a drug;

5 said process comprising the following steps:

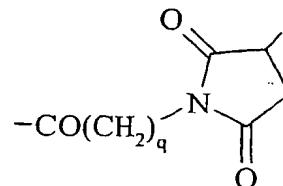
- adding to an unprotected functionalized carbon nanotube of formula I according to claim 11 or 12, an effective group or an active molecule of formula P, if appropriate protected, such as a fluorophore, such as FITC, an amino acid, a peptide, a pseudopeptide, a protein, such as an enzyme or an antibody, a nucleic acid, a carbohydrate, or a drug, or adding to an unprotected functionalized carbon nanotube of formula I according to claim 11, a group of formula Z-P, if appropriate protected, to obtain a functionalized carbon nanotube of formula I, if appropriate protected;
- if necessary, deprotecting the functionalized carbon nanotube of formula I, to obtain an unprotected functionalized carbon nanotube of formula I.

14. A process for preparing a peptide or protein functionalized carbon nanotube, of the following formula I:



5       wherein T represents a carbon nanotube and independently from each other R and R' represent H or a group of formula -M-Y-P, or of formula -M-Y-Z, provided R and R' cannot simultaneously represent -H, wherein:

- 10     ▪ -M- is a spacer group from about 1 to about 100 atoms, such as a group selected from the list comprising  $-(CH_2)_r-$  or  $-(CH_2-CH_2-O)_r-CH_2-CH_2-$ , wherein r is an integer from 1 to 20;
- 15     ▪ -Y- is a group derived from a reactive group, such as a group selected from the list comprising, -O-, -NH-, -COO-, -S-, -CH=, -CH<sub>2</sub>-, -CC<sub>k</sub>H<sub>2k+1</sub>=, wherein n is an integer from 1 to 10, in particular -CCH<sub>3</sub>=, or -CHC<sub>k</sub>H<sub>2k+1</sub>-, wherein k is an integer from 1 to 10, in particular -CHCH<sub>3</sub>-;
- 15     ▪ -Z- is a linker group, in particular a group of the following formula:



wherein q is an integer from 1 to 10;

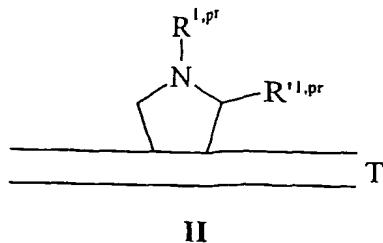
- 20     ▪ -P is a peptide, in particular of following formula:  $-[OC-CHA_i-NH]_t-H$ , wherein -A<sub>i</sub> is an amino acid side-chain, i is an integer from 1 to t and t is an integer from 1 to 150, advantageously from 1 to 50;

said process comprising the following steps:

- adding to a functionalized carbon nanotube of formula I, according to claim 11, a protected amino acid of the following formula:

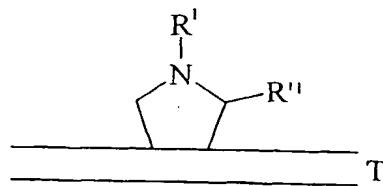


25       wherein -A<sub>i</sub> is as defined above and -Q is a protecting group to obtain a functionalized carbon nanotube of the following formula II:



wherein independently from each other R<sup>1,pr</sup> and R<sup>11,pr</sup> represent -H or a group of formula -M-Y-OC-CHA<sub>i</sub>-NH-Q, or of formula -M-Y-Z-OC-CHA<sub>i</sub>-NH-Q, wherein -M-, -Y-, -Z-, -A<sub>i</sub> and -Q are as defined above;

- deprotecting the functionalized carbon nanotube of formula II to obtain a functionalized carbon nanotube of the following formula III:



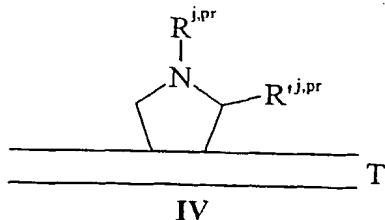
**III**

wherein independently from each other R<sup>1</sup> and R<sup>11</sup> represent -H or a group of formula -M-Y-OC-CHA<sub>i</sub>-NH<sub>2</sub>, or of formula -M-Y-Z-OC-CHA<sub>i</sub>-NH<sub>2</sub>, wherein -M-, -Y-, -Z-, and -A<sub>i</sub> are as defined above;

- adding to the functionalized carbon nanotube obtained at the preceding step a protected amino acid of the following formula:

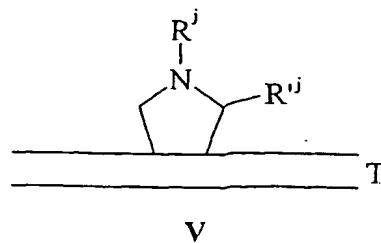


wherein -A<sub>i</sub> is as defined above and -Q is a protecting group to obtain a functionalized carbon nanotube of the following formula IV:



wherein independently from each other R<sup>j,pr</sup> and R<sup>11,j,pr</sup> represent -H or a group of formula -M-Y-[OC-CHA<sub>i</sub>-NH]<sub>j</sub>-Q, or of formula -M-Y-Z-[OC-CHA<sub>i</sub>-NH]<sub>j</sub>-Q, wherein -M-, -Y-, -Z-, -A<sub>i</sub> and -Q are as defined above, and j is an integer from 2 to t;

- deprotecting the functionalized carbon nanotube of formula IV to obtain a functionalized carbon nanotube of the following formula V:

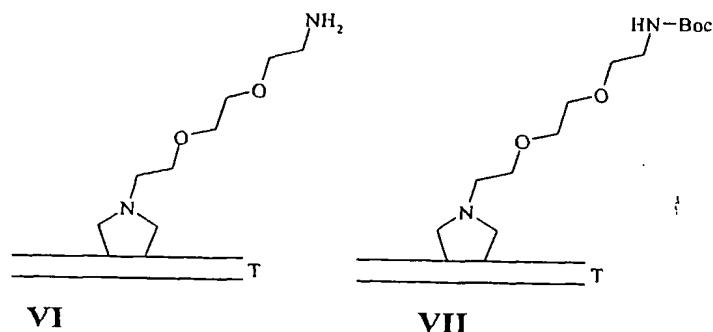


wherein independently from each other  $R^j$  and  $R'^j$  represent -H or a group of formula  $-M-Y-[OC-CHA_i-NH]_j-H$ , or of formula  $M-Y-Z-[OC-CHA_i-NH]_j-H$ , wherein  $-M-$ ,  $-Y-$ ,  $-Z-$ , and  $-A_i$  are as defined above, and  $j$  is an integer from 2 to  $t$ ;

- repeating the last two steps  $t-1$  times to obtain a peptide or protein functionalized carbon nanotube of formula I.

10 15. A process according to any of claims 12 to 14, wherein -Q is a capping group, such as  $\text{CH}_3\text{CO}-$  (acetyl), methyl, or ethyl, or a protecting group, such as a group selected from the list comprising methyl, ethyl, benzyl, *tert*-butyl, trityl, 3-nitro-2-pyridylsulfonyl, *tert*-butyloxycarbonyl (Boc), fluorenylmethyloxycarbonyl (Fmoc), benzylcarbonyl, trimethylsilylethyoxy carbonyl, phtalimide, or ethyleneoxy.

15  
16. A process for preparing a functionalized carbon nanotube of one of the following formulae VI and VII:

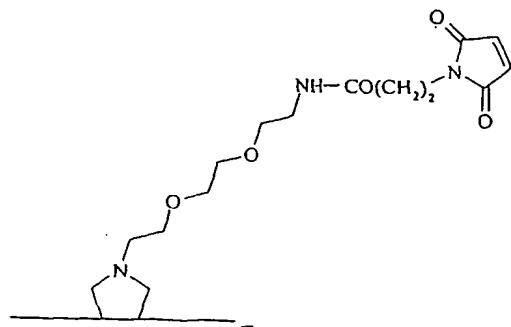


wherein T represents a carbon nanotube and Boc represents tert-butyloxycarbonyl, said process comprising the following steps:

- adding, to a carbon nanotube, the compounds  $(CH_2O)_n$  (*para*formaldehyde) and  $Boc-NH-(CH_2-CH_2-O)_2-CH_2-CH_2-NH-CH_2-COOH$  by a 1,3-dipolar cycloaddition, to obtain a protected functionalized carbon nanotube of formula VII;

- if necessary, deprotecting the protected functionalized carbon nanotube of formula VII, to obtain an unprotected functionalized carbon nanotube of formula VI.

5 17. A process for preparing a functionalized carbon nanotube of the following formula VIII:

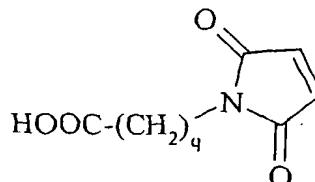


VIII

wherein T represents a carbon nanotube, said process comprising the following step:

10

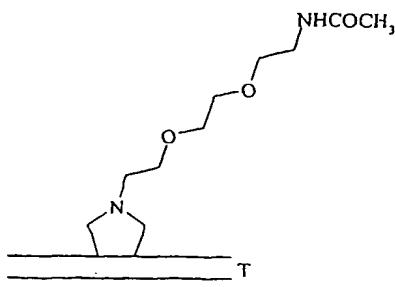
- adding, to a carbon nanotube of formula VI according to claim 16, a compound of the following formula:



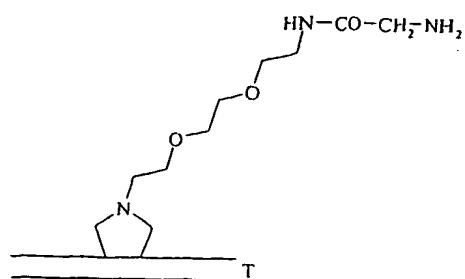
to obtain a functionalized carbon nanotube of formula VIII.

5

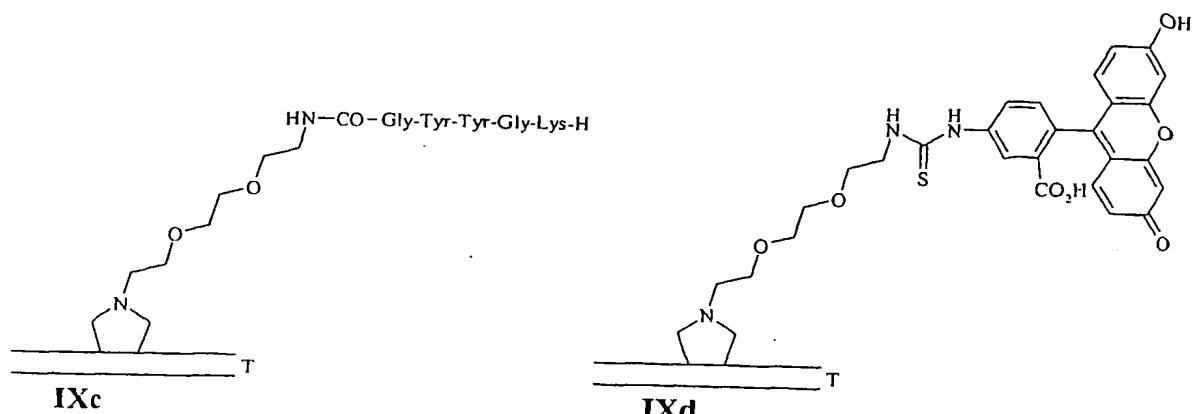
18. A process for preparing a functionalized carbon nanotube of one of the following formulae IXa, IXb, IXc, IXd, IXe, Xb and Xc:



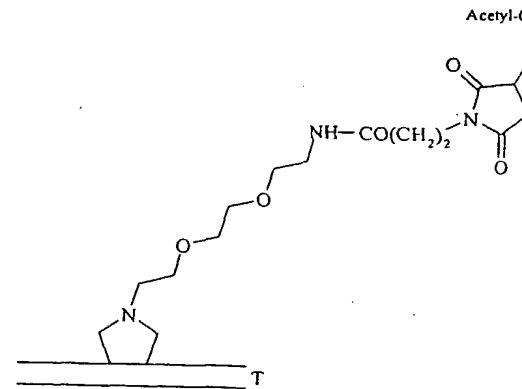
IXa



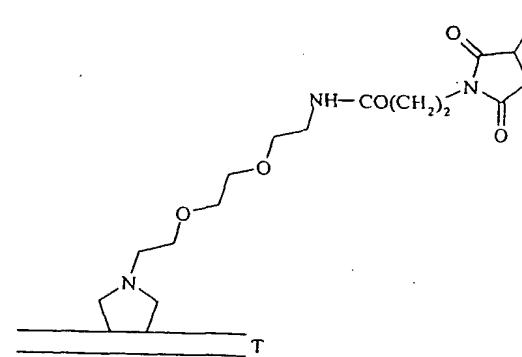
IXb



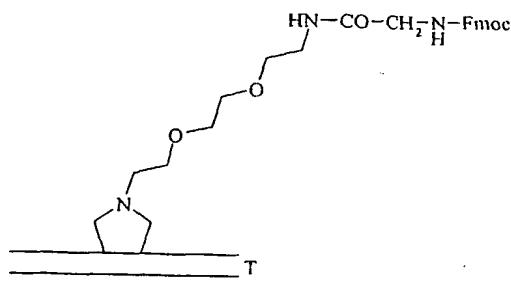
HN-CO-Gly-Tyr-Tyr-Gly-Lys-H



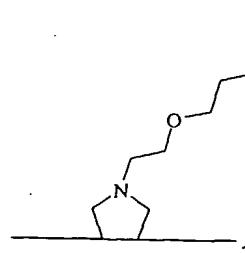
Acetyl-Cys-Gly-Ser-Gly-Val-Arg-Gly-Asp-Phe-Gly-Ser-Leu-Ala-Pro-Arg-Val-Ala-Arg-Gln-Leu-OH



5



HN-CO-CH<sub>2</sub>-N-Fmoc



HN-CO-Gly-Tyr(tBu)-Tyr(tBu)-Gly-Lys(Boc)-Boc

wherein T represents a carbon nanotube, Fmoc represents fluorenylmethyloxycarbonyl, tBu represents tert-butyl and Boc represents tert-butyloxycarbonyl, said process comprising the following steps:

- adding,
  - either to a functionalized carbon nanotube of formula VI according to claim 16, a group chosen among: CH<sub>3</sub>-COOH, Fmoc-Gly-OH, Boc-Lys(Boc)-Gly-Tyr(tBu)-Tyr(tBu)-Gly-OH, or FITC,
  - or to a functionalized carbon nanotube of formula VIII according to claim 17, the following group, Acetyl-Cys-Gly-Ser-Gly-Val-Arg-Gly-Asp-Phe-Gly-Ser-Leu-Ala-Pro-Arg-Val-Ala-Arg-Gln-Leu-OH,
- to obtain a functionalized carbon nanotube of respective formula IXa, Xb, Xc, IXd or IXe;
- if necessary, deprotecting the functionalized carbon nanotube of formula Xb or Xc to obtain respectively the functionalized carbon nanotube of formula IXb or IXc.

19. A functionalized carbon nanotube such as obtained by the process of any of claims 11 to 18.

20. A pharmaceutical composition comprising as active substance at least one functionalized carbon nanotube according to any of claims 1 to 10 or 19, in association with a pharmaceutically acceptable vehicle, such as a liposome, a cyclodextrin, a microparticle, a nanoparticle, or a cell penetrating peptide.

21. Use of a functionalized carbon nanotube according to any of claims 1 to 10 or 19, as a pharmaceutical vehicle.

22. Use of a functionalized carbon nanotube according to any of claims 1 to 10 or 19, for the delivery of drugs, in particular for the intracellular delivery of drugs.

23. Use of a functionalized carbon nanotube according to any of claims 1 to 10 or 19, for the preparation of an immunogenic composition intended to provide an immunological protection to the individual to whom it has been administrated.

24. Use of a functionalized carbon nanotube according to any of claims 1 to 10 or 19, for the preparation of a medicament intended for the treatment or the prophylaxis of cancer, autoimmune or infectious diseases.
- 5 25. Use of a functionalized carbon nanotube according to any of claims 1 to 10 or 19, for the preparation of functionalized surfaces such as plastic or glass surfaces.
26. Use of a functionalized carbon nanotube according to any of claims 1 to 10 or 19, for the preparation of electrochemical biosensors.